POROUS RESIN FILM AND INK JET RECORDING MEDIUM

FIELD OF THE INVENTION

This invention relates to a porous resin film having

5   excellent aqueous liquid or ink absorptivity and to a recording

medium comprising the porous resin film, particularly an ink

jet recording medium.

BACKGROUND OF THE INVENTION

Water-resistant synthetic papers mainly comprising

10   resins have found their use chiefly in offset printing or seal

printing using oily inks or UV-curing inks and sublimation or

melt type thermal transfer. With broadening of application,

there has been an increasing demand for synthetic papers suited

to printing with aqueous inks and application of environmentally

15   friendly aqueous pastes, that is, synthetic papers exhibiting

satisfactory absorbing properties for aqueous ink, aqueous

pastes or water as a medium thereof.

Aided by recent technical advances in multimedia, ink

jet printers have become wide spread in both business and domestic

20   use. Ink jet printers have many merits, such as adaptability

for multicolor printing, capability of forming large images,

and low printing cost. In particular, ink jet printers using

aqueous inks have supplanted those using oily inks in view of

environmental and safety considerations.

25   Ink jet printers have now found wide use as a means for

obtaining hard copies not only from word processors but from image processors as well. It has therefore been required for printed images to have more precision. Image precision depends on drying properties of ink applied to recording media. For example, when a plurality of recording sheets are printed and superposed on top of another in succession, the printed ink may cause offset to stain the image if the recording sheets have insufficient ink absorptivity.

To improve image precision, it is a commonly followed practice to coat a recording medium, such as synthetic paper, plastic film or pulp paper, with an ink receptive material containing a hydrophilic resin or inorganic fine powder (see, for example, JP-A-3-82589 and JP-A-9-216456). Ink jet recording media having an ink receptive layer mainly comprising a synthetic resin provided by thermal lamination or extrusion lamination have also been proposed (see JP-A-8-12871, JP-A-9-1920 and JP-A-9-314983). However, pulp paper coated with an ink receptive layer is liable to develop surface unevenness on the printed surface where a large amount of ink is ejected. Because plastic films coated with an ink receptive layer tend to lack enough absorptivity when a large amount of ink is ejected, the coating must have an increased thickness, requiring a number of coating operations.

Accordingly, an object of the present invention is to solve the above problems associated with the related art by

providing a porous film having satisfactory absorptivity for water as a solvent of aqueous ink or aqueous paste.

Another object of the invention is to provide a recording medium, especially an ink jet recording medium, which uniformly

5 absorbs aqueous ink without causing ink density unevenness even when solid areas are printed with a large amount of ejected ink.

SUMMARY OF THE INVENTION

As a result of extensive investigation, the present inventors have found that a porous resin film obtained from a

10 compound which is prepared by kneading a thermoplastic resin comprising a water-soluble or water-swelling hydrophilic thermoplastic resin and, if desired, an inorganic and/or an organic fine powder at a shear rate of at least 300 sec^{-1} or a laminate having the porous resin film as a surface layer exhibits

15 satisfactory absorptivity for an aqueous liquid. They have also found that a porous resin film having a liquid absorbing capacity of 0.5 ml/m^2 or more as measured in accordance with the method specified in Japan TAPPI Standard No. 51-87 is capable of absorbing ink without causing ink density unevenness even when

20 a large amount of ink is ejected and is therefore suitable as an ink jet recording medium. The present invention has been completed based on these findings.

The present invention provides a porous resin film which is obtained from a compound prepared by kneading a composition

25 comprising 30 to 100% by weight of a thermoplastic resin

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comprising a hydrophilic thermoplastic resin and 0 to 70% by weight of an inorganic and/or an organic fine powder in an intermeshing twin-screw extruder at a screw shear rate of 300 sec^{-1} or higher and which has a liquid absorbing capacity

5   of 0.5 ml/m^2 or more as measured in accordance with the method specified in Japan TAPPI Standard No. 51-87.

The present invention also provides a laminate comprising a base layer having on at least one side thereof the above-described porous resin film as a printable surface layer.

10   The present invention furthermore encompasses a liquid absorber and a recording medium comprising the porous resin film or the laminate, particularly a recording medium for ink jet recording comprising the porous resin film or the laminate and a colorant fixing layer.

15   The porous resin film of the present invention exhibits high absorptivity for an aqueous solvent or aqueous ink.   The recording medium comprising the porous resin film of the invention forms precise images free from ink density unevenness even when printed with a large amount of ink ejected from an

20   ink jet. Accordingly, the porous resin film and the recording medium of the invention are suited to a wide variety of applications including ink jet recording media.

25   DETAILED DESCRIPTION OF THE INVENTION

The compound for making the porous resin film is prepared by kneading a thermoplastic resin comprising a hydrophilic thermoplastic resin and, if desired, an inorganic and/or an inorganic powder at a screw shear rate of 300 sec^{-1} or higher, preferably 500 to 25,000 sec^{-1}, more preferably 800 to 15,000 sec^{-1}. If the screw shear rate is lower than 300 sec^{-1}, the hydrophilic thermoplastic resin is not sufficiently dispersed, resulting in poor liquid absorptivity.

The term "screw shear rate" as used herein refers to the slope of the velocity in the clearance between the outer circumference of a screw and the inner wall of the barrel of an extruder (hereinafter simply referred to as a screw clearance). While depending on the screw clearance, a screw revolution speed of 100 to 1,500 rpm generally produces a sufficient shear rate. The screw shear rate is calculated by multiplying the circumference depicted by the screw periphery by the number of revolutions per second and dividing the product by the screw clearance.

The twin-screw extruder which can be used in the present invention includes co-rotating intermeshing twin-screw ones and counter-rotating intermeshing ones, with co-rotating intermeshing twin-screw extruders being preferred.

The porous resin film has a liquid absorbing capacity of 0.5 ml/m^2 or more, preferably 3 to 2600 ml/m^2, more preferably 6 to 100 ml/m^2. For use as a recording medium to be recorded

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with aqueous ink, it is particularly preferred for the porous resin film to have a liquid absorbing capacity of 6 to 50 ml/m^2. If the liquid absorbing capacity is less than 0.5 ml/m^2, the porous resin film exhibits insufficient absorption for aqueous

5   ink or aqueous paste.   Since the liquid absorptivity of the porous resin film also depends on the film thickness, the upper limit of the liquid absorbing capacity will be decided according to end use with the film thickness taken into consideration.

     The "liquid absorbing capacity" is measured according

10   to Japan TAPPI Standard, No. 51-87 (Pater Pulp Test No. 51-87 (Bristow's method)).   In the present invention, the liquid absorptivity of a film is represented by a "liquid absorbing capacity" measured at 2 seconds (absorption time) unless otherwise specified.   The measurement is made by using a 70 wt%

15   water/30 wt% ethylene glycol mixed solvent containing about 2 parts by weight of a staining dye, such as Malachite Green, per 100 parts by weight of the mixed solvent.   The kind and the amount of the staining dye are not particularly limited as long as the surface tension of the mixed solvent is not noticeably

20   affected.   The measurement is made with, for example, a liquid absorption tester supplied by Kumagaya Riki Kogyo K.K.

     In order to prevent squeeze-out of aqueous paste, etc., it is preferred for the porous resin film to exert high liquid absorbing properties in a shorter absorption time.   It is

25   preferred for the porous resin film to achieve a liquid absorbing

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capacity of 0.8 ml/m² or more, particularly 1 to 500 ml/m², within an absorption time of 40 milliseconds.

A porous resin film having a higher rate of liquid absorption, which can be measured simultaneously with the measurement of liquid absorbing capacity, tends to give better results in absorption and drying of overprints. The porous resin film of the present invention usually shows an absorption rate of 0.02 ml/$\{m^2 \cdot (ms)^{1/2}\}$ or greater, preferably 0.1 to 100 ml/$\{m^2 \cdot (ms)^{1/2}\}$, between 20 ms and 400 ms.

It is preferred for the porous resin film to have a surface contact angle with water of 110° or less, preferably 20 to 100°, more preferably 20 to 80°. For use as an ink jet recording medium, a contact angle of 45 to 80° is preferred. The water contact angle of 110° or less is desirable for achieving a good level of penetrability for aqueous ink, aqueous paste, etc. In some cases the water contact angle is selected according to the kind of ink for optimizing the balance between spreadability of aqueous ink droplets to directions parallel to the film surface and penetrability in the film thickness direction.

The water contact angle of the film surface is measured with a commercially available contact angle meter (e.g., CA-D, supplied by Kyowa Kaimen Kagaku K.K.) 1 minute after dropping pure water on the film surface. The measurement is repeated 10 times using an intact film for every measurement to obtain an average (n=10). There is a tendency that the porous resin

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film having a smaller difference between the maximum and minimum water contact angles in the measurement repeated 10 times shows more uniformity in absorbing aqueous ink or any other liquids comprising an aqueous medium, providing higher printing quality.

5   The difference between the maximum and minimum water contact angles is within 30°, preferably within 20°, more preferably within 15°.

The porous resin film has fine pores on its surface, through which aqueous ink or any other aqueous liquid applied

10   thereto is absorbed. The number or shape of the pores existing on the porous resin film surface can be determined by electron microscopic observation. Specifically, a piece cut out of a porous resin film is fixed on a mount, gold, gold-palladium, etc. is deposited on the surface to be observed, and the pores

15   on the film surface are observed under an electron microscope (e.g., a scanning electron microscope S-2400, available from Hitachi, Ltd.) at an arbitrary magnification to identify the number, the size, and the shape of the pores. The number of pores observed in the field is converted to the number of pores

20   per unit area. The porous resin film preferably has 1×10^6 or more pores per m^2. For securing quick absorption for aqueous liquids, 1×10^8 or more pores per m^2 are preferred. For securing the surface strength, the number of pores on the surface is preferably not more than 1×10^{15}, more preferably 1×10^{12}, per

25   m^2.

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The porous resin film has a porous structure having fine pores not only on its surface but in the inside. From the standpoint of securing improved absorbing and drying properties for aqueous ink, it is preferred for the porous resin film to have a porosity of 10% or more, particularly 20 to 75%, especially 30 to 65%. A porosity of 75% or less secures satisfactory film strength. Existence of internal pores can be confirmed by observing a cut area of the film under an electron microscope.

The term "porosity" as used herein means an area ratio of voids (pores) in a cut area of a sample film observed under an electron microscope, which is represented by equation:

Porosity (%) = $(\rho_0 - \rho)/\rho_0 \times 100$

wherein ρ_0 is the true density of the porous resin film; and ρ is the density of the porous resin film.

Specifically, a porous resin film embedded in an epoxy resin is sliced with a microtome in the direction parallel to the thickness direction and perpendicular to the planar direction, and the cut area is metallized and observed under a scanning electron microscope at an arbitrary magnification suitable for observation, e.g., at 500 to 2000 times magnification, or the electron microgram of the metallized cut area is image-analyzed to obtain the porosity. In an example, the pores are traced on a tracing film as solid images, which are processed on an image analyzer (e.g., Luzex IID, supplied by Nireco Corp.) to obtain the area ratio (%) of pores.

The porosity of a porous resin film in a laminate can also be obtained by calculating the thickness and the basis weight (g/m^2) of the porous resin film from the thickness and the basis weight of the laminate and those of the layer(s) of the laminate

5   having the porous resin film removed therefrom, obtaining the density (ρ) of the porous resin film, obtaining the non-pore area density (ρ_0) from the same but non-porous composition as the porous resin film, and applying the resulting values to the above equation.

10   The shape and size of the inside pores can be observed under a scanning electron microscope at a magnification easy for observation, e.g., 200 to 2000 times magnification. The size of the inside pores is represented by an average of diameters of at least 10 inside pores measured in the planar and thickness

15   directions.

The porous resin film of the invention comprises 30 to 100% by weight of a thermoplastic resin comprising a hydrophilic thermoplastic resin and 0 to 70% by weight of an inorganic and/or an organic fine powder.

20   The thermoplastic resin can be a mixture of a hydrophilic thermoplastic resin and a non-hydrophilic thermoplastic resin or consist solely of a hydrophilic thermoplastic resin. The thermoplastic resin is preferably a mixture of a hydrophilic thermoplastic resin and a non-hydrophilic thermoplastic resin.

25   The mixture preferably comprises 5 to 100 parts by weight,

particularly 10 to 60 parts by weight, of a hydrophilic thermoplastic resin per 100 parts by weight of a non-hydrophilic thermoplastic resin.

The non-hydrophilic thermoplastic resin which can be used in the porous resin film includes polyolefin resins, such as ethylene resins (e.g., high-density polyethylene, middle-density polyethylene, and low-density polyethylene) and propylene resins; polymethyl-1-pentene, ethylene-cyclic olefin copolymers; polyamide resins, such as nylon-6, nylon-6,6, nylon-6,10, nylon-6,12, and nylon-6,T; thermoplastic polyester resins, such as ethylene terephthalate homo- or copolymers, polyethylene naphthalate, and aliphatic polyesters; and other thermoplastic resins, such as polycarbonate, atactic polystyrene, syndiotactic polystyrene, and polyphenylene sulfide. These thermoplastic resins can be used either individually or as a combination of two or more thereof.

Of these non-hydrophilic thermoplastic resins, polyolefin resins, such as ethylene resins and propylene resins, particularly propylene resins, are preferred from the standpoint of chemical resistance, low specific gravity, and cost. Suitable propylene resins include isotactic or syndiotactic homopolypropylene. Propylene copolymers comprising propylene and an α-olefin, e.g., ethylene, 1-butene, 1-hexene, 1-heptene, and 4-methyl-1-pentene, having various stereospecificity are also useful. The propylene copolymers may be bipolymers,

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terpolymers or polymers comprising four or more monomer units and may be random copolymers or block copolymers. The propylene resin is preferably used in combination with 2 to 25% by weight of a resin having a lower melting point than a propylene

5 homopolymer, such as high-density or low-density polyethylene.

The hydrophilic thermoplastic resins which can be used in the present invention are not particularly limited as long as they dissolve in water or swell with water and exhibit plasticity at room temperature or higher temperatures. Useful

10 hydrophilic thermoplastic resins include vinyl resins, such as polyvinyl alcohol and its copolymers and crosslinked products thereof, polyvinylpyrrolidone and its copolymers; acrylic resins, such as homo- or copolymers of esters of acrylic acid, methacrylic acid or maleic acid having a hydroxyalkyl group,

15 e.g., a 2-hydroxyethyl group or a 2-hydropropyl group, and crosslinked products thereof, polyacrylamide and its copolymers, hydrolyzates of acrylonitrile polymers or crosslinked acrylonitrile polymers, homo- or copolymers of acrylic acid or methacrylic acid and crosslinked products thereof, and salts

20 of these acrylic resins (e.g., sodium salts, potassium salts, lithium salts, and primary, secondary, tertiary or quaternary ammonium salts); homo- or copolymers of maleic acid and crosslinked products thereof and salts thereof (e.g., sodium salts, potassium salts, lithium salts, and primary, secondary,

25 tertiary or quaternary ammonium salts), hydrolyzates of vinyl

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acetate-methyl methacrylate copolymers; water-soluble nylon; urethane resins, i.e., water-soluble polyurethane, superabsorbent polyurethane, and thermoplastic polyurethane; polyalkylene oxide resins, such as polyethylene oxide and

5   copolymers thereof, polypropylene oxide and copolymers thereof; polyetheramide, polyether ester amide; polyvinylamine, polyallylamine, or copolymers thereof; and the like. The hydrophilic thermoplastic resins described in *Kobunshi Kako*, No. 9, pp. 32-38 (1984) are also useful.

10   Hydrophilic resins exhibiting plasticity at room temperature or higher and relatively easy to make into film are preferred. More preferred to ensure absorptivity for an aqueous solvent or aqueous ink are those resins which are capable of dissolving in water or absorbing water to become 5 or more times,

15 particularly 8 to 50 times, as heavy as its own weight (i.e., those having a water absorption (at 30 minutes) of 5 g/g or more, particularly 8 to 50 g/g) in 30 minutes at room temperature. The water absorption (at 30 minutes) as referred to here is obtained by immersing a specimen of a hydrophilic resin having

20 a thickness of about 0.1 mm which is prepared by T-die extrusion or hot pressing in distilled water at room temperature (e.g., 25°C) for 30 minutes and dividing the weight after water absorption by the weight before absorption.

        Natural resins which are easily affected by heat, such

25 as gum arabic, tragacanth gum, corn starch, wheat starch, and

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collagen, hardly withstand the temperature at which synthetic resins are melted and are not preferred.

Particularly preferred hydrophilic thermoplastic resins are polyalkylene oxide resins which have plasticity at room temperature or higher and can be molded into film with relative ease. Polyalkylene oxide resins which are preferably used in the present invention include (i) polyester type polyalkylene oxides having an ester bond, such as reaction products between an alkylene oxide and a dibasic or polybasic acid and reaction products between a polyalkylene oxide compound and a dicarboxylic acid compound or a lower alkyl ester thereof or a carboxylic acid having three or more carboxyl groups or a lower alkyl ester compound thereof, (ii) polyurethane type polyalkylene oxides having a urethane bond, such as reaction products between a polyalkylene oxide compound and a compound having two or more isocyanate groups, (iii) polyalkylene oxides having a carbonic ester bond, such as reaction products between a polyalkylene oxide compound and a dialkyl carbonate, (iv) polyalkylene oxides having an amido bond, (v) polyalkylene oxides having a urea or thiourea bond, (vi) polyalkylene oxides having a sulfide bond or a sulfonyl bond, and (vii) polyalkylene oxides having a phosphoric ester bond or a phosphorous ester bond. Preferred of them are (i) polyalkylene oxide resins having an ester bond from the standpoint of compatibility and dispersibility with the non-hydrophilic thermoplastic resins.

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The alkylene oxide includes, but are not limited to, ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, and other α-olefin oxides having up to 30 carbon atoms, with ethylene oxide, propylene

5   oxide, 1,2-epoxybutane and 1,2-epoxyhexane being preferred. These alkylene oxides can be used either individually or as a combination of two or more thereof. In using two or more alkylene oxides, they can be allowed to react either successively or simultaneously.

10   While not limiting, the polyalkylene oxide compounds preferably include homo- or copolymers of the above-described alkylene oxides having a weight average molecular weight of 5,000 to 30,000. A weight average molecular weight of 5,000 or more is desirable for film forming properties. Polyalkylene oxide

15   compounds whose weight average molecular weight is 30,000 or less are produced with satisfactory productivity because of the relatively high reaction rate in alkylene oxide addition reaction. The polyalkylene oxide compounds are obtained by addition polymerization of alkylene oxides. For example, polyalkylene

20   oxide compounds obtained by addition polymerizing an alkylene oxide to an organic compound having two active hydrogen atoms are preferably used.

The organic compounds having two active hydrogen atoms include, but are not limited to, ethylene glycol, diethylene

25   glycol, propylene glycol, dipropylene glycol, 1,4-butanediol,

1,6-hexanediol, neopentyl glycol, bisphenol A, polytetramethylene glycol, alicyclic diols, e.g., cyclohexane-1,4-dimethanol, and amines, e.g., butylamine, laurylamine, octylamine, cyclohexylamine, and aniline. These

5 compounds can be used either individually or as a combination of two or more thereof. The organic compounds having two active hydrogen atoms are preferably selected from ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, and 1,6-hexanediol.

10   The alkylene oxide to be addition polymerized with the organic compound having two active hydrogen atoms includes, but is not limited to, ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, and other α-olefin oxides having up to 30 carbon atoms. These alkylene

15 oxides can be used either individually or as a combination thereof. In using two or more alkylene oxides in combination, they are allowed to react either successively or simultaneously.

     Preferred polyalkylene oxide compounds are those prepared by addition polymerizing ethylene oxide to an organic

20 compound having two active hydrogen atoms, then addition polymerizing an alkylene oxide having 4 or more carbon atoms, and finally addition polymerizing ethylene oxide. Reaction between the polyalkylene oxide compound thus prepared and a dicarboxylic acid compound provides a polyalkylene oxide resin

25 having relatively good compatibility with non-hydrophilic

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resins, particularly polyolefin resins. A film prepared from a mixture of such a polyalkylene oxide resin and a polyolefin resin exhibits satisfactory ink absorptivity with improved absorption uniformity on printing.

5   The carboxylic acid or a lower alkyl ester compound thereof which is allowed to react with the polyalkylene oxide compound is not structurally limited provided that it has two or more, preferably two, carboxyl groups or derivatives thereof per molecule. Examples of suitable carboxylic acids and their

10   esters include aliphatic (either straight or branched), alicyclic or aromatic di- or tricarboxylic acids having 6 to 36, preferably 8 to 24, carbon atoms, and lower alkyl esters thereof. Specific examples are sebacic acid, 1,10-decamethylenedicarboxylic acid,

15   1,14-tetradecamethylenedicarboxylic acid, 1,18-octadecamethylenedicarboxylic acid, 1,32-dotriacontamethylenedicarboxylic acid, cyclohexanedicarboxylic acid, phthalic acid, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid (inclusive of

20   various isomers), 4,4'-biphenylenedicarboxylic acid, and their lower alkyl esters.

Preferred of them are saturated or unsaturated straight-chain aliphatic dicarboxylic acids having 12 to 36 carbon atoms, particularly 12 to 26 carbon atoms, especially

25   16 to 24 carbon atoms, and their lower alkyl esters. Specific

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examples of the straight-chain dicarboxylic acids having 12 to
36 carbon atoms are 1,10-decamethylenedicarboxylic acid,
1,14-tetradecamethylenedicarboxylic acid,
1,18-octadecamethylenedicarboxylic acid, and

5 1,32-dotriacontamethylenedicarboxylic acid. The lower alkyl
esters of these dicarboxylic acids include methyl esters,
dimethyl esters, ethyl esters, diethyl esters, propyl esters,
and dipropyl esters. These dicarboxylic acids and their esters
can be used either individually or as a combination of two or

10 more thereof.

Particularly preferred as a hydrophilic thermoplastic
resin are polyalkylene oxide resins having a weight average
molecular weight of 20,000 to 200,000, particularly 80,000 to
160,000, which are obtained by copolymerizing (A) a polyalkylene

15 oxide having a weight average molecular weight of 10,000 to 30,000
which is obtained by addition polymerizing (a) an alkylene oxide
comprising ethylene oxide as a major component and a minor
component selected from propylene oxide, 1,2-epoxybutane and
1,2-epoxyhexane to (b) an organic compound having two active

20 hydrogen atoms selected from ethylene glycol, diethylene glycol,
propylene glycol, dipropylene glycol, and 1,4-butanediol and
(B) an aliphatic dicarboxylic acid having 12 to 36 carbon atoms
or a lower alkyl ester thereof.

The porous resin film preferably comprises up to 70%

25 by weight of an organic and/or an inorganic powder for ensuring

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porosity. Usually having a small specific gravity, organic powder is preferably used in an amount of 3 to 50% by weight, particularly 10 to 40% by weight. Inorganic powder is preferably used in an amount of 20 to 65% by weight, particularly 40 to

5   65% by weight. Porosity increases with the amount of powder added, but the upper limit of the proportion of the powder should be 70% so as to secure the film strength.

     The inorganic powder includes, but is not limited to, heavy ground calcium carbonate, light precipitated calcium

10   carbonate, flocculated precipitated calcium carbonate, silica having various pore volumes, zeolite, clay, talc, titanium oxide, barium sulfate, zinc oxide, magnesium oxide, diatomaceous earth, silicon oxide, and inorganic composite powder composed of a hydroxyl-containing inorganic core (e.g., silica) and an

15   aluminum oxide or hydroxide shell. Heavy ground calcium carbonate, clay, and diatomaceous earth are preferred for inexpensiveness and pore forming properties in stretching.

     In order to form pores, the organic powder is selected from resins which are incompatible with the above-described

20   non-hydrophilic thermoplastic resin and have a higher melting point or glass transition point than the non-hydrophilic thermoplastic resin. Such resins include polyethylene terephthalate, polybutylene terephthalate, polyamide, polycarbonate, polyethylene naphthalate, polystyrene, homo- or

25   copolymers of acrylic ester or methacrylic ester, melamine resins,

polyphenylene sulfite, polyimide, polyether ether ketone, and
polyphenylene sulfide. Where a polyolefin resin is used as a
non-hydrophilic thermoplastic resin, polyethylene
terephthalate, polybutylene terephthalate, polyamide,
5 polycarbonate, polyethylene naphthalate or polystyrene is
preferred.

Inorganic powder is preferred to organic powder in view
of less heat generation on combustion.

The inorganic or organic powder preferably has an average
10 particle size of 0.01 to 20 μm, particularly 0.1 to 10 μm,
especially 0.5 to 10 μm. Particles of 0.01 μm or greater are
easy to mix with the hydrophilic thermoplastic resin and the
non-hydrophilic thermoplastic resin. Particles of 20 μm or
smaller hardly cause troubles in stretching, such as sheet
15 cutting or reduction in surface strength.

The particle size of the inorganic or organic powder
can be obtained as, for example, a 50% diameter in a cumulative
distribution measured with, for example, a laser diffraction
type particle size analyzer Microtrack, supplied by Nikkiso Co.,
20 Ltd. The size of the particles dispersed by melt-kneading in
a thermoplastic resin can be obtained as an average of at least
10 particles on a cut area of the porous film observed under
an electron microscope.

The fine powder to be used can be of a single material
25 or a combination of two or more materials selected from the

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above-described organic or inorganic powders. A combination of an organic powder and an inorganic powder is also useful.

In compounding the powder with the thermoplastic resins, additives can be added if desired. Useful additives include

5   dispersants, antioxidants, compatibilizers, flame-retardants, UV stabilizers, and colorants. Where the porous resin film is for consumer durables, addition of an antioxidant, a UV stabilizer, etc. is recommended. In using organic powder, since the state of the powder is governed by the kind and amount of

10   a compatibilizer used in combination, selection of the compatibilizer is of importance. Preferred compatibilizers include epoxy-modified polyolefins and maleic acid-modified polyolefins. The compatibilizer is preferably added in an amount of 0.5 to 10 parts by weight per 100 parts by weight of

15   the organic powder.

When the hydrophilic thermoplastic resin is mixed with the non-hydrophilic thermoplastic resin and/or the inorganic and/or organic powder by melt kneading or a like method, addition of a dispersion improver is effective to improve dispersibility

20   or dispersion stability and to reduce the difference between the maximum and the minimum surface contact angles thereby to make aqueous liquid absorption more uniform. Useful dispersion improvers include polar resins, such as epoxy-containing resins (e.g., an ethylene-glycidyl methacrylate copolymer, an

25   ethylene-vinyl acetate-glycidyl methacrylate copolymer,

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glycidyl methacrylate-grafted polypropylene, and an epoxidized polybutadiene polymer), acid-modified polyolefins (e.g., maleic acid-modified polypropylene), hydroxyl-containing polyolefins (e.g., 2-hydroxyethyl methacrylate-grafted

5   polypropylene), and amino-modified polyolefins (e.g., dimethylaminoethyl methacrylate-grafted polypropylene); and organic phosphorus compounds, such as phosphite compounds (e.g., bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-t-butyl-4-methylphenyl)pentaerythritol

10   diphosphite, distearylpentaerythritol diphosphite, and bis(nonylphenyl)pentaerythritol diphosphite) and phosphonite compounds (e.g., tetrakis(2,4-di-t-butylphenyl)-4,4'-bisphenylene diphosphonite).

15   For improving ink absorptivity, the polar resin type dispersion improver is usually added in an amount of 0.1 part by weight or more, preferably 0.5 to 30 parts by weight, more preferably 1 to 15 parts by weight, per 100 parts by weight of the non-hydrophilic thermoplastic resin, and the phosphorus type

20   dispersion improver is usually used in an amount of 0.01 part by weight or more, preferably 0.1 to 5 parts by weight, still preferably 0.2 to 3 parts by weight, per 100 parts by weight of the non-hydrophilic thermoplastic resin.

The above-described components constituting the porous

25   resin film are compounded at a mixing temperature and time chosen

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according to the properties of the components. For example,
the components as dissolved or dispersed in a solvent are mixed
together, or the components are melt-kneaded. Melt kneading
achieves high productivity. Melt kneading is carried out by

5   dry blending powdered or pelletized thermoplastic resins,
inorganic and/or organic powder and an agent for giving
hydrophilicity in a Henschel mixer, a ribbon blender, a
supermixer, etc. and melt-kneading the blend in a twin-screw
extruder, extruding the molten mixture into strands, which are

10   pelletized by hot cutting or cold cutting with a strand cutter.
Alternatively, the agent for giving hydrophilicity, which can
be in the form of powder, liquid or a solution in water or an
organic solvent, is previously mixed with the thermoplastic resin
or inorganic and/or organic powder and then compounded with other

15   components.

The screw diameter of the twin-screw extruder is subject
to variation from 10 mm to 310 mm. The barrel length, which
is also subject to variation, is generally such that the L/D
ratio is about 60 at the most. The screws generally have

20   alternating conveying zones and kneading zones. In the
conveying zones the raw material is forwarded from each kneading
zone. The kneading zone usually has a double-flighted or single-,
triple- or four-flighted kneading element. A screw shear rate
of 300 to 25,000 sec^{-1} or more is produced in the twin-screw

25   extruder having a screw clearance of 0.1 to 0.4 mm operated at

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a screw revolution speed of 100 to 1,500 rpm.

The thickness of the porous resin film is not particularly limited and can vary, for example, from 10 to 400 μm, preferably from 30 to 100 μm.

5   The porous resin film of the present invention can serve as it is or be combined with another thermoplastic film, laminated paper, pulp paper, nonwoven fabric, woven fabric, etc. to form a laminate. The thermoplastic film that can be laminated with the porous resin film of the invention includes transparent or

10   opaque films of polyesters, polyamides, polyolefins, etc. In particular, the porous resin film is combined with appropriate functional layers to give recording media as demonstrated in Examples hereinafter given.

More specifically, a recording medium can be obtained

15   by laminating a thermoplastic resin film as a base layer with the porous resin film of the invention as a surface layer. The recording medium having the porous resin film as a surface layer is especially suited for ink jet recording. The base layer includes, but is not limited to, a film comprising a polypropylene

20   resin and inorganic fine powder. Such a recording medium composed of the porous resin film of the invention and other film suitably has a total thickness of about 50 μm to 1 mm.

The porous resin film and the recording medium according to the present invention can be produced by an appropriate

25   combination of various techniques known to one skilled in the

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art. Whatever method may be used, the porous resin film and the recording medium satisfying the conditions of the present invention are included in the scope of the present invention.

The porous resin film having a liquid absorbing capacity
5   of 0.5 ml/m^2 or more can be produced by any of known film formation techniques or any combination thereof. For example, stretching, calendering, blowing using a blowing agent, a method using voids-containing particles, solvent extraction, and a method comprising extracting a mixed component by dissolution can be
10 utilized. A stretching method is preferred of these techniques.

In producing a laminate comprising a base layer and the porous resin film by stretching, a stretched or unstretched base layer can be laminated with a stretched porous resin film, or a laminate composed of the base layer and the porous resin film
15 can be stretched. The latter method is simpler and more economical and enjoys more ease in controlling the porosity of both the porous resin film and the base layer. Where the laminate is for use as a recording medium, it is desirable to control stretching so that the porous resin film may have more pores
20 than the base layer to serve as a surface layer with improved ink absorptivity.

Stretching can be carried out by various known methods, such as longitudinal stretching making use of peripheral speed difference among stretching rolls, lateral stretching using an
25 oven tenter, inflation of a tubular film by use of a mandrel,

and simultaneous biaxial stretching by a combination of an oven tenter and a linear motor. The stretching temperature for non-crystalline resins is set above the glass transition temperature of the thermoplastic resin used, and that for

5 crystalline resins is set between the glass transition temperature of the non-crystalline portion and the melting point of the crystalline portion. The stretching ratio is appropriately decided according to the end use of the porous resin film or the laminate thereof, the characteristics of the

10 thermoplastic resins used, and the like. In case of using, for instance, a propylene homo- or copolymer as a non-hydrophilic thermoplastic resin, a suitable stretching ratio in uniaxial stretching is about 1.2 to 12, preferably 2 to 10, and that in biaxial stretching is about 1.5 to 60, preferably 10 to 50, in

15 terms of area ratio. In using other thermoplastic resins, a suitable stretching ratio in uniaxial stretching is 1.2 to 10, preferably 2 to 7, and that in biaxial stretching is 1.5 to 20, preferably 4 to 12, in terms of area ratio.

If necessary, heat treatment at high temperature can

20 be carried out. The stretching temperature is preferably 2 to 160°C lower than the melting point of the non-hydrophilic thermoplastic resin used. In using a propylene homo- or copolymer as a non-hydrophilic thermoplastic resin, a preferred stretching temperature is 2 to 60°C lower than the melting point

25 of the polymer, and a preferred stretching speed is 20 to

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350 m/min.

As previously stated briefly, the stretched porous resin film of the present invention can be used either as such or as a laminate with a base layer. The base layer which can be combined

5   with includes transparent or opaque resin films, such as a polyester film, a polyamide film, and a polyolefin film, plastic boards, pulp paper, nonwoven fabric, cloth, wood plates, metal plates, and so forth.

The resin films as a base layer can comprise a resin

10   and inorganic and/or organic fine powder. The resin of the base layer can comprise one or more resins selected from the aforementioned non-hydrophilic thermoplastic resins or a combination of at least one of the aforesaid non-hydrophilic thermoplastic resins and at least one of the aforesaid

15   hydrophilic thermoplastic resins. The composition of the base layer can be the same as that of the porous resins film. The resin film as a base layer may be either a stretched film or a non-stretched film.

The resin film comprising the non-hydrophilic

20   thermoplastic resin and the hydrophilic thermoplastic resin as a base layer preferably contain 5 to 100 parts by weight of the hydrophilic thermoplastic resin per 100 parts by weight of the non-hydrophilic thermoplastic resin. A practical example of the resin film as a base layer comprises 40 to 85% by weight

25   of the thermoplastic resin and 15 to 60% by weight of inorganic

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and/or organic powder. The inorganic and/or organic powder can be the same or different from that used in the surface layer (porous resin film). The inorganic and/or organic powder in the base layer can have an average particle size of 0.1 to 10 μm,

5   preferably 0.6 to 3 μm.

While not limiting, the thickness of the base layer usually ranges from 5 to 100 μm, preferably from 20 to 500 μm. The thickness of the laminate is not limited and can arbitrarily be selected according to the use, generally ranging from 15 to

10   2000 μm, preferably 20 to 500 μm, still preferably 25 to 350 μm.

If desired, the porous resin film and the laminate comprising the porous resin film can be subjected to a surface oxidation treatment to improve surface hydrophilic properties, absorbing properties, affinity to an ink fixing agent or an ink

15   receptive layer (hereinafter described), and adhesion to a base layer. Effective surface oxidation treatments include a corona discharge treatment, a flame treatment, a plasma treatment, a glow discharge treatment, an ozone treatment, and the like. A corona discharge treatment and a flame treatment are preferred.

20   A corona discharge treatment is more preferred.

A corona discharge treatment is carried out at a discharge energy of 600 to 12,000 J/m^2 (10 to 200 $W.min/m^2$), preferably 1,200 to 9,000 J/m^2 (20 to 150 $W.min/m^2$). At least 600 J/m^2 is required for attaining sufficient effects. A

25   discharge energy exceeding 12,000 J/m^2 will produce no further

effects. A flame treatment is performed at an energy of 8,000 to 200,000 J/m^2, preferably 20,000 to 100,000 J/m^2. At least 8,000 J/m^2 is required for attaining appreciable effects. An energy exceeding 200,000 J/m^2 will produce no further effects.

5   Where the porous resin film or the laminate having the porous resin film as a surface layer is used as a recording medium, a colorant fixing layer for fixing a dye or a pigment or an ink receptive layer can be formed on the surface thereof. A colorant fixing layer or an ink receptive layer provided on the porous

10   resin film having high water absorptivity is more effective than on a resin film having poor absorptivity in reducing feathering and improving absorptivity. Further, it is feasible to reduce the thickness of the colorant fixing layer or the ink receptive layer compared with the thickness required for a resin film having

15   poor absorptivity. The colorant fixing layer has functions of rounding ink dots to make an image clearer and preventing a colorant from running due to water or humidity. Accordingly, it is particularly useful where the porous resin film is used as an ink jet recording medium.

20   The color fixing layer or ink receptive layer is formed by coating or transfer. A cationic hydrophilic resin and fine powder are preferably used to improve colorant fixing properties. For example, cationic copolymers having a cationic group, such as an amino group, a modified amino group or a quaternary ammonium

25   base, in the main chain or side chain thereof can be used.

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The ink receptive layer for ink jet recording includes a porous ink-receptive layer mainly comprising a pigment and an aqueous binder, which is used where ink is required to dry quickly, and a swelling ink-receptive layer mainly comprising
5   an aqueous binder, which is used where high gloss is demanded.

The pigment includes synthetic silica, colloidal silica, alumina hydrosol, aluminum hydroxide, talc, calcium carbonate, clay, plastic pigments, barium sulfate, and titanium dioxide, with porous synthetic silica and alumina hydrosol being preferred.
10   The aqueous binder includes aqueous emulsions of polyurethane resins, polyester resins, vinyl acetate resins, acrylic ester resins, styrene-acrylic ester copolymers, vinyl acetate-acrylic ester copolymers, styrene-butadiene copolymers, and methyl methacrylate-butadiene copolymers; and
15   water-soluble polymers, such as polyvinyl alcohol, ethylene-vinyl alcohol copolymers having a silanol group, polyvinyl acetal, polyvinylpyrrolidone, methylethyl cellulose, sodium polyacrylate, starch derivatives, and gelatin derivatives. Polyvinyl alcohol or an ethylene-vinyl alcohol
20   copolymer having a silanol group is preferred when combined with synthetic silica or alumina hydrosol.

Where the ink receptive layer is required to have ink fixing properties, an ink setting agent is incorporated. The ink setting agent includes cationic polymers, such as a tertiary
25   ammonium salt of polyethyleneimine, an acrylic copolymer

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comprising a quaternary ammonium group as a copolymer component, and an epichlorohydrin adduct of polyaminepolyamide.

If desired, the colorant fixing layer or ink receptive layer can contain pigment dispersing agents, thickeners,

5 defoaming agents, fluorescent whitening agents, UV absorbers, antioxidants, antiseptics, waterproofing agents, and the like.

The porous ink-receptive layer preferably comprises 50 to 90% by weight of the pigment, 10 to 40% by weight of the aqueous binder, and 0 to 20% by weight of the ink setting agent. The

10 swelling ink-receptive layer preferably comprises 60 to 100% by weight of the aqueous binder and 0 to 40% by weight of the ink setting agent.

The ink receptive layer is formed by general coating techniques, such as blade coating, rod coating, wire bar coating,

15 slide hopper coating, curtain coating, air knife coating, roll coating, and size pressing. The coating weight of the ink receptive layer is usually 0.05 to 100 g/m^2, preferably 0.1 to 50 g/m^2, while varying with required levels of ink absorptivity and gloss, the absorbing properties of the substrate, and the

20 like. The ink receptive layer can have a single layer structure or a multiple layer structure. Two or more layers making up the ink receptive layer may have the same or different compositions and can be formed either simultaneously or successively.

25 The porous resin film of the invention can be printed

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by not only ink jet printing but other printing methods with no particular restrictions. Specifically, gravure printing using ink comprising a known vehicle having a pigment dispersed therein and other known printing methods such as aqueous

5   flexographic printing and screen printing are applicable. The porous resin film is also printable by metal deposition, gloss printing, matte printing, etc. Patterns to be printed are selected arbitrarily from concrete patterns (e.g., animals, scenes, checks, polka dots) and abstract patterns.

10   The porous resin film is useful as well in the fields demanding absorptivity for aqueous liquids. Such applications include adhesive labels with aqueous self-adhesive, labels for containers such as bottles and cans, water-absorbing films, wallpaper, decorative paper of plywood or plasterboard,

15   anti-fogging films, drip-proof wrapping paper for food, coasters, paper for handicrafts, paper for *origami*, water retentive sheets, sheets for protecting soil from drying, assisting materials for concrete drying, desiccants, dehumidifiers, and so forth.

    The present invention will now be illustrated in greater

20   detail with reference to Examples, Comparative Examples, and Test Examples. The quantities, ratios, operations and the like hereinafter described are subject to modification within the scope and the spirit of the present invention. Accordingly, it should be understood that the present invention is not

25   construed as being limited to these Examples. Unless otherwise

noted, all the parts and percents are by weight.

EXAMPLE 1

Preparation of base layer and longitudinal stretching:

Composition A consisting of 75% of polypropylene having

5   a melt flow rate (MFR; 230°C, 2.16 kg load) of 1 g/10 min, 5%

of high-density polyethylene having an MFR (190°C, 2.16 kg load)

of 8 g/10 min, and 20% of calcium carbonate having an average

particle size of 3 µm was melt-kneaded in an extruder set at

250°C, extruded into strands, and cut into pellets.

10   The resulting compound A was extruded from an extruder

set at 250°C through a T-die, and the extruded sheet was chilled

on a chill roll to obtain an unstretched sheet. The unstretched

sheet was heated to 140°C and longitudinally stretched 4.5 times

to obtain a stretched sheet.

15   In melt-kneading resin components or a mixture of resin

components and fine powder in this and other Examples, 0.2 part

of 4-methyl-2,6-di-t-butylphenol (antioxidant) and 0.1 part of

Irganox 1010 (phenolic antioxidant, available from Ciba-Geigy

Ltd.) were added per 100 parts of the total of the resin components

20   and the powder.

Formation of porous resin film laminate (recording medium):

Composition B consisting of 30% of polypropylene having

an MFR of 5 g/10 min (hereinafter abbreviated as PP1), 12% of

a polyalkylene oxide resin (an ester of (i) an ethylene oxide

25   (about 90%)-butylene oxide (about 10%) copolymer having a weight

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average molecular weight of about 20,000 and (ii)

octadecamethylenedicarboxylic acid; water absorption (at 30

minute): 14 g/g; hereinafter abbreviated as PEPO1), and 58% of

calcium carbonate having an average particle size of 3 μm

5   (hereinafter abbreviated as CC1) was melt kneaded in a twin-screw

extruder TEX65 (screw diameter: 65 mm) having a screw clearance

of about 0.4 mm at a screw shear rate of 3000 sec^{-1} to prepare

compound B.

Compound B was extruded from an extruder set at 240°C

10   (temperature a).   The extruded sheet was superposed on each side

of the above-prepared 4.5-fold stretched sheet, and the laminate

was cooled to 55°C (temperature b).   The laminate was heated

to 156°C (temperature c) and stretched 8 times in the lateral

direction by means of a tenter, annealed at 157°C temperature

15   d), and cooled to 50°C (temperature e), followed by trimming

to obtain a porous resin film laminate (recording medium)

composed of a surface absorbing layer B (70 μm)/base layer A

(40 μm)/back absorbing layer B (20 μm) having a total thickness

of 130 μm.

20   The particle size of the calcium carbonate powder used

in Examples is a cumulative 50% diameter measured with Microtrack

(laser diffraction type particle size analyzer, supplied by

Nikkiso Co., Ltd.).

Evaluation:

25   The following evaluation was carried out on the surface

absorbing layer B side of the laminate.

(1) Liquid absorbing capacity

The liquid absorbing capacity was measured according to Japan TAPPI Standard, No. 51-87 (Pater Pulp Test No. 51-87 (Bristow's method) with a liquid absorption tester supplied by Kumagaya Riki Kogyo K.K. by using a water/ethylene glycol mixed solvent (70/30 by weight) containing 2 parts of Malachite Green as a staining dye per 100 parts of the mixed solvent. The liquid absorbing capacity at 2 seconds of the porous resin film was 7.3 ml/m^2.

(2) Average contact angle with water and maximum-minimum difference of water contact angle

The water contact angle of the surface of the porous resin film was measured with a contact angle meter CA-D, supplied by Kyowa Kaimen Kagaku K.K. 1 minute after dropping pure water on the film surface. The measurement was repeated 10 times using an intact film for every measurement to obtain an average (n=10) and a difference between the maximum and the minimum contact angles.

(3) Confirmation of surface pores and measurement of the number of surface pores

A cut piece of the porous resin film was observed to confirm the existence of pores on the surface and on the cut area. A piece cut out of an arbitrary part of the porous film was fixed on a mount. The surface to be observed was metallized

and observed under a scanning electron microscope S-2400, supplied by Hitachi, Ltd., at 500 times magnification to confirm existence of pores on the surface. Further, the electron microscopic image was output on heat-sensitive recording paper or photographed. The number of the pores on the surface was found to be about $1.0 \times 10^9/m^2$.

(4) Confirmation of internal pores and measurement of internal porosity

The porous resin film laminate was embedded in an epoxy resin and sliced with a microtome in the direction parallel to the thickness direction and perpendicular to the planar direction. The cut area was metallized and observed under a scanning electron microscope S-2400, supplied by Hitachi, Ltd., at 2000 times magnification to confirm existence of internal pores (voids).

The microscopic image of the observed field was output on heat-sensitive recording paper, and the thickness of each layer was measured. The total thickness and the total basis weight (g/m^2) of the laminate were measured. The surface absorbing layer was stripped off over a given area, and the thickness and basis weight of the remaining film were measured. From the differences were obtained the thickness and basis weight (g/m^2) of the porous resin film, and the basis weight was divided by the thickness to give the density (ρ) of the absorbing layer. Separately, compound B was pressed into a 1 mm thick sheet at 230°C, and the density (ρ_0) was measured. The porosity was

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calculated according to equation:

$$\text{Porosity (\%)} = (\rho_0 - \rho)/\rho_0 \times 100$$

wherein ρ_0 is the true density of the porous resin film; and ρ is the density of the porous resin film.

5 (5) Ink absorptivity

Color charts for evaluation (2 cm by 2 cm; printed in monochrome at 50% or 100% density; or overprinted at 200% density) were prepared and reproduced on the recording medium (surface layer of the porous resin film laminate) by ink jet printing

10 using an ink jet printer JP2115, supplied by Graphtec Corp., and pigment inks (yellow, magenta, cyan, and black). Filter paper was pressed onto the printed area at regular intervals to see whether ink was transferred to the filter paper. The time when the ink was no more transferred was recorded. The

15 ink absorptivity of the absorbing layer was evaluated according to the following rating system.

6 ... The ink is not transferred immediately after printing.

5 ... The ink is not transferred after 1 minute or

20   shorter from printing.

4 ... The ink is not transferred after 2 minutes or shorter from printing.

3 ... The ink is not transferred after 3 minutes or shorter from printing.

25 2 ... The ink is not transferred after 4 minutes or

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shorter from printing.

1 ... The ink is not transferred after 5 minutes or
shorter from printing.

0 ... The ink does not dry and is transferred after more
than 5 minutes from printing.

Further, the printed area after ink absorption was
observed with the naked eye to evaluate density unevenness
according to the following rating system.

4 ... No density unevenness is observed.

3 ... Little density unevenness is observed.

2 ... Density unevenness is observed.

1 ... Appreciable density unevenness is observed.

Feathering after ink absorption was observed with the
naked eye and rated as follows.

4 ... The image is clear with no feathering.

3 ... The image has little feathering and is
distinguishable almost satisfactorily.

2 ... The image has feathering to impair
distinguishability.

1 ... The image is useless, suffering from considerable
feathering.

After completion of printing, the printed sheets were
allowed to stand in a room for 1 hour. After the standing, the
printed surface was observed with the naked eye to see whether
surface unevenness developed, which was rated as follows.

3 ... The printed surface is even with non-printed area.

2 ... The printed sheet has little surface unevenness.

1 ... The printed sheet has appreciable surface unevenness.

5   The results of evaluation are shown in Table 1 below.

COMPARATIVE EXAMPLE 1

A porous resin film and a laminate thereof were prepared and evaluated in the same manner as in Example 1, except for using 40% of PP-1 as a non-hydrophilic thermoplastic resin and

10   60% of CC1 as fine powder in place of composition B. The porous resin film scarcely absorbed water at 2 seconds so that its liquid absorbing capacity was regarded to be 0 ml/m^2. The results of other evaluation items are shown in Table 1.

COMPARATIVE EXAMPLE 2

15   A porous resin film and a laminate thereof were prepared and evaluated in the same manner as in Example 1, except that 30% of PEPO1 as a hydrophilic thermoplastic resin and 70% of PP-1 as a non-hydrophilic thermoplastic resin were used in place of composition B and that tentering of the laminate was not carried

20   out. The resulting resin film scarcely absorbed water at 2 seconds so that its liquid absorbing capacity was regarded to be 0 ml/m^2. The results of other evaluation items are shown in Table 1.

EXAMPLES 2 TO 5

25   A porous resin film and a laminate thereof were prepared

and evaluated in the same manner as in Example 1, except for changing the screw shear rate of the twin-screw extruder (TEX65 or TEX30) as shown in Table 1. The results of evaluation are shown in Table 1.

5   EXAMPLE 6

A porous resin film and a laminate thereof were prepared and evaluated in the same manner as in Example 1, except that a composition consisting of 40% of PEP01 as a hydrophilic resin and 60% of PP-1 as non-hydrophilic thermoplastic resin was

10   kneaded in a twin-screw extruder TEM47 having a screw diameter of 47 mm and a screw clearance of about 0.2 mm at a screw shear rate of 5000 sec^{-1} and that temperatures a to e were changed as shown in Table 1. The results of evaluation are shown in Table 1.

15

COMPARATIVE EXAMPLE 3

A porous resin film and a laminate thereof were prepared and evaluated in the same manner as in Example 1, except for changing the screw shear rate of the twin-screw extruder (TEX30;

20   screw diameter: 30 mm) to 100 sec^{-1}. The results of evaluation are shown in Table 1.

EXAMPLE 7

A mixture of 75% of polypropylene having an MFR of 1 g/10 min and 5% of high-density polyethylene having an MFR

25   (190°C, 2.16 kg load) of 10 g/10 min was mixed with 20% of CCl

(inorganic powder), and the blend was kneaded in an extruder, extruded into strands, and pelletized to obtain compound C.

A mixture of 40% of PP1, 10% of PEPO1 resin, and 50% of CC1 was melt kneaded in a twin-screw extruder TEX65 set at a temperature of 230°C at a screw shear rate of 2200 sec^{-1} to prepare compound D in the form of pellets.

Compound C and compound D were melted in separate extruders, laminated in the same T-die, co-extruded, and chilled to obtain an unstretched laminate sheet having a layer of compound D on both sides of a layer of compound C. The sheet was heated to 143°C and stretched 4.5 times in the longitudinal direction, followed by cooling. The stretched sheet was again heated to 154°c (temperature c) and stretched 8 times in the lateral direction by means of a tenter, annealed at 155°C (temperature d), chilled to 50°C (temperature e), and trimmed to obtain a porous resin film laminate composed of a surface absorbing layer D (50 μm)/base layer C (30 μm)/back absorbing layer D (30 μm) having a total thickness of 110 μm.

The resulting laminate was evaluated in the same manner as in Example 1. The results obtained are shown in Table 1.

TABLE 1

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Comp. Ex. 3	Ex. 7
Hydrophilic Thermoplastic Resin: Kind	PEPO1	-	PEPO1	PEPO1	PEPO1	PEPO1	PEPO1	PEPO1	PEPO1	PEPO1
Water absorption (at 30 sec) (g/g)	14	-	14	14	14	14	14	14	14	14
Amount (%/part)	12/43	-	30/43	12/43	12/43	12/43	12/43	40/67	12/43	10/25
Non-hydrophilic Thermoplastic Resin: Kind	PP1	PP1	PP1	PP1	PP1	PP1	PP1	PP1	PP1	PP1
Amount (%/part)	30/100	40/100	70/100	30/100	30/100	30/100	30/100	60/100	30/100	40/100
Fine Powder: Kind	CC1	CC1	-	CC1	CC1	CC1	CC1	-	CC1	CC1
Particle size (μm)	3	3	-	3	3	3	3	-	3	3
Amount (%)	58	60	-	58	58	58	58	-	58	50
Kneading Step: Twin-screw extruder	TEX65	TEX65	TEX65	TEX65	TEX65	TEX65	TEX30	TEX47	TEX30	TEX65
Screw clearance (mm)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.2	0.4	0.4
Screw shear rate (1/sec)	3000	3000	3000	8500	5000	800	400	1850C	100	2200
Molding Step: Temperature a (°C)	240	240	240	240	240	240	240	240	240	-
Temperature b (°C)	55	55	50	55	55	55	55	55	55	55
Temperature c (°C)	156	155	-	156	156	156	156	154	156	154
Temperature d (°C)	157	155	-	157	157	157	157	155	157	155
Temperature e (°C)	50	50	-	50	50	50	50	50	50	50
Thickness of Laminate (μm)	130	146	356	130	130	130	130	110	130	110
Thickness of Surface Layer (μm)	70	65	70	70	70	70	70	40	70	50
Thickness of Base Layer (μm)	40	40	255	40	40	40	40	40	40	30
Liquid Absorbing Capacity at 2 second (ml/m²)	7.3	0	0	8.0	7.6	6.5	5.8	5.6	2.2	7.2
Average Water Contact Angle (°)	90	115	33	88	90	93	95	76	93	96
Difference between Max. and Min. Water Contact Angles (°)	7	3	5	4	9	13	19	9	40	6
Internal Porosity (%)	58	50	0	58	58	58	58	48	40	63
Number of Surface Pores (/m²)	1.0E+9	2.2E+10	0	1.0E+9	1.0E+9	1.0E+9	1.0E+9	9.2E+9	7.6E+8	7.6E+9
Ink Absorptivity: Monochrome 50%	6	0	0	6	6	6	6	6	4	6
Monochrome 100%	6	0	0	6	6	6	5	6	3	6
Overprint 200%	6	0	0	6	6	6	4	6	1	6
Density Unevenness	4	1	1	4	4	4	3	4	1	4
Feathering	3	1	1	3	3	3	3	3	1	3
Surface Unevenness after Printing	3	3	3	3	3	3	3	3	3	3

EXAMPLE 8

Both sides of the laminate prepared in Example 1 were subjected to a corona discharge treatment at an energy of 4800 J/m^2 (80 W·min/m^2). The treated laminate was evaluated in
5 the same manner as in Example 1. The results obtained are shown in Table 2 below.

COMPARATIVE EXAMPLE 4

Both sides of the laminate prepared in Comparative Example 1 were subjected to a corona discharge treatment at an
10 energy of 4800 J/m^2 (80 W·min/m^2). The treated laminate was evaluated in the same manner as in Example 1. The results obtained are shown in Table 2 below.

EXAMPLE 9

One side (surface absorbing layer B) of the laminate
15 prepared in Example 1 was subjected to a corona discharge treatment at an energy of 4800 J/m^2. The treated side was coated with an ink receptive coating composition having the following formulation to a coating weight of 5 g/m^2 on a solid basis, dried, and supercalendered to obtain ink jet recording paper.

20 Ink receptive coating composition:

Synthetic silica powder (Mizucasil P-78D, available from Mizusawa Industrial Chemicals, Ltd.)   100 parts

Polyvinyl alcohol (PVA-117, available from Kuraray Co., Ltd.)   30 parts

25   Polyaminepolyamide-epichlorohydrin adduct (WS-570,

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available from Japan PMC Corp.)   10 parts

Sodium polyacrylate (reagent grade, available from Wako

Pure Chemical Industries, Ltd.)   5 parts

Water   1600 parts

5   The resulting recording paper was evaluated in the same

manner as in Example 1.   The results obtained are shown in Table

2.

EXAMPLE 10

One side (surface absorbing layer B) of the laminate

10   prepared in Example 1 was subjected to a corona discharge

treatment at an energy of 4800 J/m^2.   The treated side was coated

with an ink receptive coating composition having the following

formulation to a coating weight of 5 g/m^2 on a solid basis and

dried to obtain ink jet recording paper.

15   Ink receptive coating composition:

Alumina sol (Alumina Sol 100, available from Nissan

Chemical Industries, Ltd.; solid content: 10%)100 parts

Polyvinyl alcohol (PVA-117, available from Kuraray Co.,

Ltd.)   10 parts

20   Water   100 parts

The resulting recording paper was evaluated in the same

manner as in Example 1.   The results obtained are shown in Table

2.

EXAMPLE 11

25   Ink jet recording paper was prepared and evaluated in

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the same manner as in Example 10, except for using the following

ink receptive coating composition.   The results obtained are

shown in Table 2.

Ink receptive coating composition:

5   Urethane binder (SF Coating 8310, available from

            Dainippon Ink & Chemicals, Inc.; solid content: 13%)

                                                100 parts

            Polyamidine (Himax SC700L, available from Hymo Co.,

            Ltd.; solid content: 30%)   2 parts

                        COMPARATIVE EXAMPLE 5

10   Commercially available ink jet recording paper having

a pulp paper base (MJA4SP1 exclusive for Epson Superfine) was

evaluated in the same manner as in Example 1.   The results are

shown in Table 2.

TABLE 2

	Example 8	Compara. Example 4	Example 9	Example 10	Example 11	Compara. Example 5
Base or Substrate	Example 1	Compara. Example 1	Example 1	Example 1	Example 1	pulp-based paper for ink jet printer
Surface Oxidation Treatment	corona treatment	corona treatment	corona treatment	corona treatment	corona treatment	
Surface Oxidation Energy (J/m²)	4800	4800	4800	4800	4800	
Liquid Absorbing Capacity (at 2 sec) after Surface Oxidation Treatment (ml/m²)	7.4	0	7.4	7.4	7.4	
Water Contact Angle after Surface Oxidation Treatment (°)	58	75	58	58	53	
Difference between Max. and Min. Water Contact Angles after Surface Oxidation Treatment (°)	4	3	4	4	4	
Solid Content of Ink Receptive Layer (g/m²)	-	-	5	5	5	
Ink Absorptivity: 50% Monochrome	6	0	6	6	6	6
100% Monochrome	6	0	6	6	6	6
200% Overprint	6	0	6	6	6	6
Density Unevenness	4	3	4	4	4	4
Feathering	3	1	4	4	4	4
Surface Unevenness after Printing	3	3	3	3	3	1

As is apparent from the results shown in Tables 1 and 2, the porous resin films according to the present invention exhibit extremely excellent ink absorptivity, causing no density unevenness even where the ink is ejected in large quantities.

5 The comparative films whose liquid absorption is out of the range specified in the present invention (Comparative Examples 1 and 2) show poor ink absorbing properties. The film of Comparative Example 3, in which the screw shear rate in melt kneading was out of the range specified in the present invention, caused

10 density unevenness.

As is apparent from the results of Examples 9 to 11, the porous films having an ink receptive layer exhibit excellent ink absorptivity, demonstrating the effects of the present invention. Comparisons between Examples and Comparative

15 Example 5 clearly reveal that the porous films of the invention do not develop surface unevenness after printing.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications

20 can be made therein without departing from the spirit and scope thereof.